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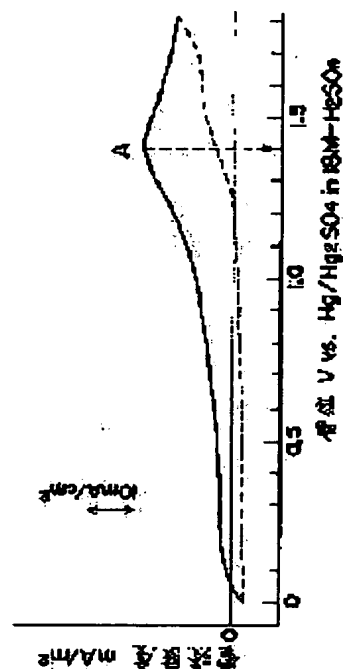
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## (54) CARBON ELECTRODE AND METHOD AND DEVICE FOR ELECTROLYZING HF-CONTAINING FUSED SALT BY USING THIS ELECTRODE

(57)Abstract:

PURPOSE: To provide the carbon electrode which eliminates the danger of destruction (by the formation of an intermetallic compd.) in the joint part with the terminal part for energization to the anode of the electrolyzing device and the danger of local destruction and slow partial peeling (by lack of mechanical strength) at the time of using the carbon electrode as the anode for electrolysis of an HF-contg. fused salt.

CONSTITUTION: This carbon electrode consists of a porous carbon block and has 50MPa bending strength. The peak having the max. current density in a single sweep voltamogram determined by the potential scanning at 5mV/sec potential scanning speed in concd. sulfuric acid at 25° C is shown by  $\geq 1.2V$  potential with mercuric sulfate as a reference electrode.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The carbon electrode which shows the peak which has the maximum current density in the single-sweep-operation voltamogram for which it consists of a porous carbon block, and flexural strength is 50 or more MPas, and it asked by the potential scan of potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid to the potential beyond 1.2V by using the mercury as a reference electrode.

[Claim 2] The carbon electrode according to claim 1 where this carbon block is characterized by having in pore at least one sort of metal fluorides chosen from LiF, NaF, CsF, AlF<sub>3</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, and NiF<sub>2</sub>.

[Claim 3] The electrolysis approach that it is in the electrolysis approach of HF content fused salt characterized by electrolyzing a carbon electrode according to claim 1 or 2 for the electrolytic bath which consists of HF content fused salt as an anode plate, and this HF content fused salt is a KF-HF system, a CsF-HF system, a NOF-HF system, a KF-NH<sub>4</sub>F-HF system, or a NH<sub>4</sub>F-HF system.

[Claim 4] The electrolytic device which is in the electrolytic device of HF content fused salt which includes a cell and an anode plate, and cathode, and is characterized by this anode plate being a carbon electrode according to claim 1 or 2.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the electrolysis approach of HF content fused salt and electrolytic device which use a carbon electrode and it. Furthermore, it not only excels in the mechanical strength in detail, but it is chemically stable, and in HF content molten salt electrolysis exposed to the fluorine ambient atmosphere which accompanies HF, the intercalation compound generation by which knowledge was newly carried out to it being one cause of a crack cannot break out easily, electrolysis actuation is made to perform in the stable condition, and it is related with a carbon electrode useful although a product with high purity is moreover manufactured. This invention relates to the electrolysis approach of HF content fused salt and equipment which are characterized by using the above-mentioned carbon electrode as an anode plate again.

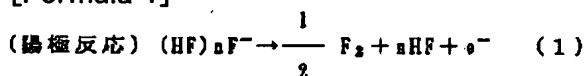
[0002]

[The trouble which a Prior art and invention tend to solve] Electrolysis manufacture of a fluorine is mentioned as a typical example of the electrolysis approach of HF content fused salt. Generally as a manufacturing method of a fluorine, the moderate temperature method which electrolyzes in current and about 90-degree C mixed fused salt of a potassium fluoride and hydrogen fluoride is adopted.

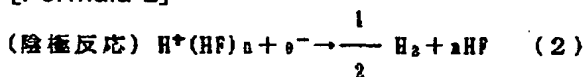
[0003] The bath presentations in a moderate temperature method are KF and 2HF, and the reason this is used widely has the low vapor pressure of HF near the melting point, and is for the melting point of a bath to be unable to change easily also due to fluctuation of HF concentration under bath moreover. As an anode plate of a cell, since a metal cannot be used by anodic dissolution, carbon is chiefly used as electrode material. As cathode, on research level, although iron, steel, nickel, Monel, etc. are used, industrially, iron is used from acquisition ease and economical efficiency, and electrolysis is usually performed by current density 7 - 13 A/dm<sup>2</sup>, and bath voltage 8.5-15V.

[0004] The electrode reaction in the anode plate and cathode in this electrolysis approach is expressed as follows.

[Formula 1]



[Formula 2]



It is known that the following difficult problems will follow on the carbon electrode used in electrolysis manufacture of such a fluorine.

[0005] (b) Although the terminal area for energization to the anode plate in an electrolytic device is usually carrying out junction immobilization of the end of a carbon electrode with a copper bolt and a copper nut, big destruction of a carbon electrode takes place in this part during

electrolysis.

[0006] (b) Generally a porous carbon electrode has few mechanical strengths, and during electrolysis, the collapse local also in a location and the gradual partial exfoliation of those other than the fixed portion to the terminal area for energization to the above-mentioned anode plate occur, and it produces detailed carbon powder (in here). "Gradual partial exfoliation" reacts easily with a fluorine, and serves as CF<sub>4</sub>, and this which means that a carbon electrode breaks gradually in the form of omission of the carbon particle from a front face mixes it into the fluorine as a product.

[0007] (c) By the reaction of F<sub>2</sub> and a carbon anode plate produced on a carbon anode plate during electrolysis, fluoride graphite with very low surface energy generates. In the part which the fluoride graphite on a carbon anode plate generated, \*\*\*\* with a bath worsens and serves as inactive electrochemically. The effective area of an electrode decreases according to increase of the coverage of the electrode surface by fluoride graphite, and true current density increases. This is the main causes of the anode plate overvoltage in fluorine electrolysis, and if the coverage by fluoride graphite exceeds 20%, a sudden rise of an electrical potential difference will be observed and it will become energization impossible. This phenomenon is called the anode effect and poses a big problem in the industrial electrolytic decomposition process of HF content fused salt.

[0008] About the anode effect of (Ha), this invention persons have succeeded in the ability of the metal fluoride which contains lithium fluoride in the pore of a carbon block to already be controlled by sinking in effectively among these troubles (JP,2-47297,A).

[0009] However, the problem (namely, the big destruction and the local collapse by the fixed portion of a carbon electrode, and gradual partial exfoliation) of the above-mentioned (\*\*) and (\*\*) is not yet solved, but is a fatal thing in actual electrolysis operation of HF content fused salt. Therefore, in order to enable electrolysis of HF content fused salt stabilized [ long duration ] and to obtain the product of a high grade, development of a carbon electrode without the risk of these destruction and collapse, and exfoliation was desired eagerly.

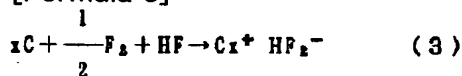
[0010]

[Means for Solving the Problem and its Function] Generally, a carbon electrode grinds petroleum coke and pitch coke, uses them as the aggregate, adds a coal-tar pitch and synthetic resin to this as a binding material, and consists of kneading and a porous carbon block calcinated [ is fabricated and ] and acquired. Under the present circumstances, graphite microcrystal has the field where some aligned in a certain direction, it grows up and the aggregate corks used progress while heat treatment temperature becomes [ this ] high.

[0011] Knowledge carried out [ leading to destruction of the carbon-electrode part by which junction immobilization of the lack of the mechanical strength with which this invention persons are represented by flexural strength as a result of research was carried out at the terminal area for energization to the anode plate separated and located in the upper part of an electrolytic bath in the case of electrolysis operation of the chemical behavior of the graphite structure field which local destruction of a carbon electrode and gradual partial exfoliation were brought about, and also the carbon electrode at the time of electrolysis described above of HF content fused salt, and ].

[0012] That is, this invention persons found out between the arranged graphite layers being able to extend, an intercalation compound arising by the reaction shown in (3) types, carbon material expanding remarkably with generation of an intercalation compound, as a result of an interlayer spacing's becoming large, and resulting in destruction, when the carbon electrode was put into F<sub>2</sub> ambient atmosphere where HF was accompanied.

[Formula 3]



[0013] In order that this invention persons may lose local destruction or collapse of the problem of big destruction of the carbon electrode by generation of this intercalation compound and the carbon electrode under electrolysis, and gradual partial exfoliation The above-mentioned problem

that the carbon electrode which satisfies two requirements that a peak is shown in the potential more than specific level in the single-sweep-operation voltamogram which has the flexural strength more than specific level, and was called for by the potential scan under specific conditions accompanies the conventional carbon electrode is solvable wholeheartedly as a result of research. Also unexpectedly the knowledge of the ability to use it for stable operation of electrolysis of HF content fused salt and manufacture of a high grade product advantageously as an anode plate is carried out, and this invention is reached.

[0014] Therefore, when the 1st purpose of this invention is used for electrolysis of HF content fused salt as an anode plate, it is offering a carbon electrode without the risk of the destruction in a part for a joint with the terminal area for energization to the anode plate in an electrolytic device, and the risk of local destruction and gradual partial exfoliation. [0015] Moreover, stable electrolysis operation is possible for the 2nd purpose of this invention, and it is offering the electrolysis approach of HF content fused salt using the above-mentioned carbon electrode as an anode plate a high grade product's being obtained.

[0016] Moreover, the 3rd purpose of this invention is offering the electrolytic device of HF content fused salt which does not need to exchange the carbon electrode as an anode plate and enables electrolysis of long duration by using the above-mentioned carbon electrode as an anode plate.

[0017] The above of this invention and many other purposes, many descriptions, and many profits will become clear from detailed explanation and the detailed aforementioned claim of an attached drawing and the following.

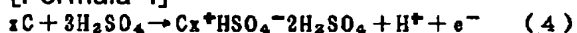
[0018] That is, according to this invention, it consists of a porous carbon block and the carbon electrode which shows the peak which has the maximum current density in the single-sweep-operation voltamogram for which flexural strength is 50 or more MPas, and it asked by the potential scan of potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid to the potential beyond 1.2V by using the mercury as a reference electrode is offered.

[0019] Hereafter, the description of the carbon electrode of this invention is explained. If the graphite crystal growth in carbon material exceeds the amorphous part surrounding the field as for which graphite microcrystal carried out orientation exceeding a carbon particle, it cannot happen easily. So, if aggregate corks are pulverized even to several microns or dozens of microns, comparatively a lot of pitch binders are added to this and carbon material is made [ that the orientation of the graphite microcrystal under organization can be controlled, and ] [ whether the corks of a fine mosaic structure are used for the aggregate, and ] Or graphite crystal growth could be restricted by using a particle raw material like mesophase microbeads with a particle size of several microns, and the knowledge of the ability of the generation reaction of the intercalation compound which showed the carbon block with which graphite crystal growth was restricted by the above-mentioned (3) formula not to occur easily was carried out. Of course, as for the heat treatment temperature for baking for generating a carbon block, it is desirable to be carried out at low temperature as much as possible so that graphite crystal growth may not be urged.

[0020] The difficulty nature of the intercalation compound generation about a carbon block can be judged in the single-sweep-operation voltamogram (linear sweep voltammogram) for which it asked into concentrated sulfuric acid from the potential (as a reference electrode, the 2nd mercury electrode of a sulfuric acid is used) which shows the peak at which this carbon block has the maximum current density. In addition, the above-mentioned peak corresponds to the 1st stage intercalation compound generation reaction of carbon and a sulfuric acid.

[0021] The graphite lamellar compound generation reaction of the carbon material in the inside of concentrated sulfuric acid is shown by the following (4) types.

[Formula 4]



[0022] (4) In case an intercalation compound arises by the reaction of a formula, it must extend between graphite layers, and while performing the potential scan for asking for a single-sweep-operation voltamogram, concentrated sulfuric acid diffuses it between graphite layers as layer

invasion matter. If development of graphite microcrystal is bad, the activation energy to the process of expansion between the above-mentioned graphite layers and diffusion of the layer invasion matter will become large, and the potential for generating a graphite lamellar compound becomes \*\* as compared with what graphite microcrystal is good and progressed. That is, the carbon electrode cannot make an intercalation compound easily, so that it is \*\*\*\* in the potential in which the peak (this peak corresponds to the 1st stage intercalation compound generation with carbon and a sulfuric acid) which has the maximum current density in a single-sweep-operation voltamogram appears.

[0023] It is indispensable that set to the electrode of this invention and the peak which has the maximum current density in the single-sweep-operation voltamogram for which it asked by the potential scan by potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid is shown in the potential beyond 1.2V by using the mercury as a reference electrode (a carbon electrode often writes from this the potential which shows this peak as "summit potential"). As mentioned above, this peak corresponds to generation of the 1st stage intercalation compound of carbon and a sulfuric acid. The check of generation of the 1st stage intercalation compound can be performed by a stop's investigating a potential scan and investigating a carbon electrode in an X diffraction, when this peak is reached. It can begin by satisfying the requirements this summit potential of whose is more than 1.2V, and comparatively big destruction [namely, the problem of said (b)] of the carbon electrode resulting from expansion by generation of an intercalation compound can be lost during electrolysis operation. Summit potential is more than 1.3V preferably.

[0024] Moreover, the local destruction by lack of the mechanical strength of the carbon electrode under electrolysis stated to said (b) or collapse, and gradual partial exfoliation make a minute carbon block and carbon powder float in an electrolytic bath, since they have large surface area while this is activity, will react with F<sub>2</sub> gas easily, will generate gas CF<sub>4</sub>, and they will mix it into a request product, F<sub>2</sub> [ for example, ]. It is required for preventing this for the carbon material which constitutes a carbon electrode to be the thing of high intensity mechanically. Therefore, as for the carbon electrode of this invention, it is indispensable to have the flexural strength of 50 or more MPas. 55 or more MPas of flexural strength of the carbon electrode of this invention are 80 or more MPas still more preferably preferably.

[0025] In order to obtain the carbon material which satisfies the two above-mentioned indispensable requirements For example, [ whether it is made to increase the amount of the binder corks which add same weight or the pitch binder beyond it to fines-like aggregate corks mostly, and share the role of association, and ] Or [ whether the eburnation of carbon material is achieved using the aggregate in which large contraction is shown in a heat treatment phase like the corks of a minute mosaic structure, or raw coke, and ] Or it can attain by using the 1 yuan system ingredient with which the aggregate and binding material like a deterioration pitch or mesophase microbeads were constituted in one.

[0026] The size says the mosaic what is being distributed uniformly [ a thing 10 micrometers or less ] in an isotropic matrix in the process which the minute mosaic structure which says here heats a pitch, and a mesophase microsphere generates. If carbon material with such structure is heated, a mosaic part will be contracted greatly and a high density ingredient will be obtained.

[0027] Moreover, the so-called mesophase microbeads obtained by separating the mesophase microsphere generated from the pitch as mentioned above remain as it is, and can be advantageously used as a raw material of the carbon electrode of this invention as a system ingredient. [ of 1 yuan ]

[0028] If ambient atmosphere control is performed in case a pitch is distilled dryly, in air, in non-graphitized-carbon material and nitrogen gas, the precursor of easily-graphitized-carbon material can be obtained, these can be said to be a deterioration pitch, and 1 yuan can be too used for manufacture of the carbon electrode of this invention as a system ingredient. [0029] That is, the carbon electrode of this invention can be manufactured by starting the carbon material from which particle size heat-treats the 2 yuan system ingredient which blended the pitch binder about 80 to 130 weight section like a coal-tar pitch and a petroleum pitch with the aggregate corks 100 weight section in which the shape of fines which is 3-20 micrometers carried out

temporary quenching, or a 1 yuan system ingredient like a deterioration pitch or mesophase microbeads, and is obtained in the shape of a block etc. 1000 degrees C – 1500 degrees C of heat treatment temperature are usually 1000 degrees C – 1200 degrees C preferably also from the purpose of generation prevention of the intercalation compound under the mechanical strength desired and electrolysis. Thus, although the acquired carbon block is porosity, compared with the conventional carbon electrode, it has precise structure. That is, porosity is about 2% to about 10%, and the average aperture of pore is very small, for example, is about 1 micrometer.

[0030] the mechanical property of the carbon material of the carbon electrode of this invention – the flexural strength -- with -- \*\*\*\* -- it can display. When it measures according to the approach of JIS R7222 by 40–80mm three-point test [ distance bending ] between the supporting points (a sample is supported with the two supporting points and a load is placed upside down in the center between the supporting points), as for the flexural strength of the carbon electrode of this invention, it is indispensable that 50 or more MPas are shown. 55 or more MPas of flexural strength are 80 or more MPas still more preferably preferably. When using the carbon electrode which has such flexural strength for the anode plate of HF content molten salt electrolysis (for example, electrolysis of KF–HF system fused salt, such as KF–2HF for fluorine manufacture), generating of CF<sub>4</sub> can be suppressed to trace extent.

[0031] As described above, it is indispensable requirements to satisfy two conditions that the peak which has the maximum current density in the single-sweep-operation voltamogram for which the carbon electrode of this invention showed the flexural strength of 50 or more MPas, and it asked by the potential scan by potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid is shown in the potential beyond 1.2V by using the 2nd mercury of a sulfuric acid as a reference electrode. It will not set without satisfying both of these two conditions to electrolysis of HF content fused salt. Both generating of a big crack and the local destruction thru/or collapse in a joint with the terminal area for energization to an anode plate, and generating of gradual partial exfoliation can be decreased remarkably. Manufacture of stable electrolysis operation and a high grade product is enabled, and if at least one of the two requirements of these is not satisfied, the purpose of this invention cannot be attained.

[0032] In the desirable mode of this invention, a carbon electrode has at least one sort of metal fluorides by which \*\* ON was further carried out to the pore of a porous carbon block for the aforementioned anode effect control. As a suitable metal fluoride, LiF, NaF, CsF, AlF<sub>3</sub>, MgF<sub>2</sub>, CaF<sub>2</sub>, NiF<sub>2</sub>, etc. can be mentioned. These metal fluorides can be introduced even if independent [ in the pore of a carbon block ] under the conditions of elevated-temperature high pressure. However, it is desirable to perform installation of a metal fluoride in the form of the mixture of two or more sorts of metal fluorides from a viewpoint which performs installation to the pore of a carbon block easily and effectively. The surface tension of the metal fluoride mixture which fused the reason is because it is smaller than the surface tension of each fused metal fluoride. As desirable combination of a metal fluoride, the combination of AlF<sub>3</sub> and NaF and the combination of LiF and NaF can be mentioned especially. 1 is desirable [ about 3// by the 1 to about 3/2, and LiF/NaF system ] generally, although especially a mole ratio is not limited at an AlF<sub>3</sub>/NaF system respectively about 2/from 1 about 0.5/. The thing with desirable using NaF combining other metal fluorides is because NaF can remove the effect which is not desirable as for a ferric ion by reacting easily with the second iron (it not being desirable in order that the elution of the iron from the iron instrument of an electrolytic device may generate this and it may give viscosity to an electrolytic bath) of fluoride, forming a complex (NaFFeF<sub>3</sub>) and settling it.

[0033] If at least one sort of metal fluorides are infiltrated into a carbon block, \*\* ON of the metal fluoride will be carried out into the detailed pore of a carbon block. Also unexpectedly, the knowledge of flexural strength of the carbon block into which at least one sort of metal fluorides were infiltrated improving sharply was carried out. [0034] The method of making it filled up with a metal fluoride (or mixture) into the pore of a carbon block will not be limited, especially if the filling factor to the inside of the pore of a carbon block can be preferably filled up still more preferably at least 50% at least 30% so that it may become 65% or more.

[0035] For example, according to the approach of the predetermined temperature after



introducing a molten-metal fluoride (or mixture) into pore, heating a metal fluoride (or mixture) more than the melting point, carrying out contact coexistence with a carbon block in the state of melting, and putting a pressure predetermined to a contact coexistence system, usually cooling a carbon block even to a room temperature, sinking-in press fit can be carried out easily in the pore of a carbon block of a metal fluoride (or mixture). Under the present circumstances, the filling factor of the metal fluoride in the pore of a carbon block (or mixture) can be adjusted by controlling the pressure put on a contact coexistence system.

[0036] The above-mentioned approach is explained still more concretely. For example,  $\text{AlF}_3\text{-NaF}$  system metal fluoride mixture is prepared so that the mole ratio of  $\text{AlF}_3/\text{NaF}$  may be set to 3:1. the inside of it after it heated this mixture at 970–1050 degrees C and it carried out melting enough in the crucible — a carbon block — putting in (it being put into a crucible, before a carbon block carries out heating fusion of the metal fluoride mixture) — the press means of carbon material — using — mixed melting — as it is immersed in the inside of the body, it fixes to it. This crucible is put into a pressurized container. After nitrogen gas or argon gas next permutes this interior of a container, a temperature up is carried out to about 1000 degrees C at a rate of about 5–10 degrees C / min, and then this container is decompressed to 10 – 50mmHg. This reduced pressure actuation prevents oxidation of this ingredient while it removes air and makes sinking-in press fit actuation easier than the pore in a carbon block. After it did in this way and the metal fluoride mixture and the carbon block which were fused have next carried out contact coexistence, inert gas, for example, nitrogen, or an argon is introduced in this container, and internal pressure is held by 50 to 100kg/cm<sup>2</sup> for about 30 minutes to about 2 hours. Then, if this carbon block is taken out from a pressurized container and carries out natural radiationnal cooling in atmospheric air, the carbon electrode of this invention of a desirable mode where the metal fluoride mixture of an  $\text{AlF}_3\text{-NaF}$  system consists of a carbon block by which \*\* ON was carried out into pore can be obtained.

[0037] If it means the rate (%) that the pore is filled up with the metal fluoride (or mixture), and A and true specific gravity are set into A', and the filling factor (X) of a metal fluoride (or mixture) sets porosity to P for the bulk specific gravity of a carbon block of a base material and the specific gravity of a metal fluoride (or mixture) restoration electrode is set to B when making the amount of the pore under carbon block into 100%, it will be called for by formula  $B=A+XPA'$ . Porosity can be measured by the mercury porosimeter.

[0038] HF content fused salt can be electrolyzed into stability by using the carbon electrode of this invention.

[0039] Therefore, according to this invention, further, it is in the electrolysis approach of HF content fused salt characterized by electrolyzing the above-mentioned carbon electrode for the electrolytic bath which consists of HF content fused salt as an anode plate, and the electrolysis approach that this HF content fused salt is a  $\text{KF-HF}$  system, a  $\text{CsF-HF}$  system, a  $\text{NOF-HF}$  system, a  $\text{KF-NH}_4\text{F-HF}$  system, or a  $\text{NH}_4\text{F-HF}$  system is offered.

[0040] In the approach of this invention, the electrolysis product obtained when HF content fused salt is a  $\text{KF-HF}$  system (preferably  $\text{KF-2HF}$  salt), a  $\text{CsF-HF}$  system, or a  $\text{NOF-HF}$  system (preferably  $\text{NOF-3HF}$  salt) is a fluorine, and when HF content fused salt is a  $\text{KF-NH}_4\text{F-HF}$  system or a  $\text{NH}_4\text{F-HF}$  system, the electrolysis product obtained is 3 nitrogen fluoride. It not only can electrolyze HF content fused salt into stability, but according to the approach of this invention, it can obtain a desired electrolysis product by the high grade.

[0041] Moreover, according to this invention, it is in the electrolytic device of HF content fused salt which includes a cell and an anode plate, and cathode further, and the electrolytic device characterized by this anode plate being the above-mentioned carbon electrode is offered. Although it will not be limited especially if, as for the ingredient of the cathode in the electrolysis approach of this invention, and an electrolytic device, a hydrogen overvoltage cannot make a fluoride easily low, iron cathode is industrially used from a viewpoint of acquisition ease and economical efficiency.

[0042] The equipment of this invention is explained in more detail later, referring to to drawing 3 and drawing 4. [0043] The following experiments were conducted in order to prove the surprising effectiveness of this invention. As an example, the coal-tar pitch of 90 weight sections

was added to the temporary-quenching petroleum coke powder 100 weight section ground below to 325 meshes (Tyler), about 150–250 degrees C of volatile matter were adjusted while carrying out long duration kneading under heating in about 180–220 degrees C preferably, and it ground again after cooling, fabricated from [below 100-mesh (Tyler)] \*\*, it calcinated at 1000 degrees C, and the carbon block was made [a sample (I)].

[0044] On the other hand, the coal-tar pitch of 50 weight sections was mixed to the aggregate corks 100 weight section in the same aggregate corks as the above ground below to 325 meshes (Tyler), except it, kneading, grinding, and shaping were performed by the same technique as the above, it heat-treated at 2800 degrees C after that, and the carbon block was acquired [a sample (II)].

[0045] Samples (II) were 46MPa(s) although the sample (I) showed the bending strength of 57MPa(s).

[0046] Single-sweep-operation Volta MUMETORI was performed by potential scan speed 5 mV/sec at 25 degrees C among 18M concentrated sulfuric acid about these carbon material. The mercury electrode which it is immersed in a platinum plate in cathode, and made the reference electrode immersed into concentrated sulfuric acid in both cases was used.

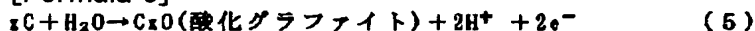
[0047] The result (namely, single-sweep-operation voltamogram) obtained about a sample (I) and (II) was shown in drawing 1 and drawing 2, respectively. In 1000-degree-C baking material [a sample (I)], the 1st stage intercalation compound generation peak (A) and (summit potential) were observed by 1.4V so that drawing 1 might show. Moreover, with the ingredient [a sample (II)] which the amount of binders heat-treated at 2800 degrees C few so that drawing 2 might show, the 1st stage intercalation compound generation peak (B) and (summit potential) were observed by 0.9V.

[0048] Although destruction of an ingredient was not seen even if it continued the potential scan 50 times among 1.5V from 0, with the sample (II) and the (conventional technique), in the 1st scan, it swelled up from the edge of carbon material by (C) at the time of 1.05V, the part immersed in concentrated-sulfuric-acid liquid expanded greatly, and, as for a sample (I) and (this invention), the electrode destroyed potential.

[0049] Next, using the two above-mentioned kinds of prepared carbon material as an electrode, it electrolyzed with the galvanostatic process in the electrolytic bath for fluorine manufacture, and the performance evaluation of an electrode was performed. That is, the griddle (160x100mm, two sheets) was used for the carbon material (250x70x15mm) and cathode which were prepared in the anode plate using KF and 2HF bath to the electrolytic bath. During electrolysis, the bath was kept at 90 degrees C, blew anhydrous fluoric acid into the bath suitably, and maintained the bath presentation at the constant value of KF and 2HF.

[0050] In order to perform stable operation in the case of electrolysis, it is important to perform sufficient dehydration of a bath and to devise the assembly of the terminal area for energization to an anode plate, and to prevent invasion to a part for this terminal area of F<sub>2</sub>, HF, or a bath. If water is during a bath, carbon and the oxygen which is the discharge product of water will react, and oxidation graphite will be produced. Oxidation graphite reacts easily by the unstable matter with the fluorine atom produced with the electrode, and turns into stable fluoride graphite. For this reason, even if slight water exists during a bath (about 500 ppm), if it energizes, it will become easy to produce fluoride graphite, an inactive part will increase electrochemically according to the increment in the coverage of this, true current density will rise, and an anode plate overvoltage will increase as that result. These reactions are shown in (5) and (6) types.

[Formula 5]



[Formula 6]



[0051] So, in order to remove the water under bath enough, the nickel electrode was used, it electrolyzed by the low current consistency, and the fluorine was generated, and water was removed besides the system by the reaction of the following (7) types.

$2F_2 + H_2O \rightarrow OF_2 + 2HF$  (7)

[0052] Moreover, while inserting a flexible graphite sheet in the contact parts of the metal of the terminal area for energization to an anode plate, and a carbon electrode and reducing contact resistance on the occasion of energization, invasion into this part of a bath, or  $F_2$  and  $HF$  was prevented.

[0053] The following electrolysis operation was performed after the above housekeeping operation.

[0054] When the sample (II) and the (ingredient whose summit potential in the single-sweep-operation voltamogram which was prepared with the burning temperature of 2800 degrees C, and for which flexural strength is 46MPa(s) and it asked under said conditions is 0.9V) were made into the anode plate and electrolysis with constant current was carried out by 7 A/dm<sup>2</sup>, it destroyed in the part to which the carbon electrode touches the part and busbar which are immersed in  $KH$  and  $2FH$  bath in 14 days. During electrolysis, when  $CF_4$  contained in generation fluorine gas was measured by the gas-chromatography method and the infrared-absorption-spectrum method, it was always 500 ppm or more.

[0055] On the other hand, when the sample (I) and the (ingredient whose summit potential in the single-sweep-operation voltamogram which was prepared with the burning temperature of 1000 degrees C, and for which flexural strength is 57MPa(s) and it asked under said conditions is 1.4V) were made into the anode plate and electrolysis with constant current was carried out by 7 A/dm<sup>2</sup>, there was no destruction of an electrode for 70 days. Moreover,  $CF_4$  in fluorine gas was also very as low as an average of 20 ppm.

[0056] Thus, while the electrode of this invention enables electrolysis operation the resistance over a crack is remarkable, high resistance and stable, it is very useful as an electrode for electrolysis manufacture of the fluorine aiming at a high grade fluorine without mixing of  $CF_4$ .

[0057] Prolonged electrolysis can be performed without being able to control the amount of mixing of  $CF_4$  to the inside of a fluorine, and moreover an electrode causing a crack and destruction, if electrolysis manufacture of the fluorine is carried out in  $KF$  and  $2HF$  electrolytic bath by this invention, using the carbon material which satisfies both of two conditions that flexural strength is 50 or more MPas, and summit potential is more than 1.2V in the single-sweep-operation voltamogram for which it asked under said conditions as an anode plate as stated above. Therefore, the carbon electrode of this invention has the big advantage in electrolysis of  $HF$  content fused salt.

[0058] The carbon electrode of this invention is applicable to an electrolytic device as shown in drawing 3 and drawing 4. Drawing 3 is the outline sectional view of the electrolytic device of this invention showing the interior [ like ] 1 voice, and drawing 4 is the outline sectional view which met the IV-IV line of drawing 3. In drawing 3 and drawing 4, 1 uses the anode plate of this invention in cathode, and 2 uses iron. Moreover, in order to prevent mixing of  $F_2$  and  $H_2$ , the skirt board (3) which covered Monel metal to mild steel or mild steel is prepared. It uses, in order that  $F_2$  outlet, five  $H_2$  outlet, and 6 ( drawing 3 ) may keep four at  $HF$  feed hopper and 7 may keep a cell at 80-90 degrees C in a warm water jacket. Moreover, 8 ( drawing 4 ) is the flexible graphite sheet inserted in the terminal area for energization to an anode plate, and while preventing invasion into a bath or this part of  $F_2$  and  $HF$ , the function as packing for stress relaxation and the function of increase prevention of contact resistance are also demonstrated. 9 shows the oil level of  $HF$  content fused salt electrolytic bath at the time of electrolysis.

[0059] Moreover, the carbon electrode of this invention can be applied in favor of electrolysis composition of  $NF_3$ , and  $HF$  content fused salt is a  $KF-NH_4F-HF$  system electrolytic bath and a  $NH_4F-HF$  system electrolytic bath in this case.  $NF_3$  is used as gas for washing of the gas for dry etching gas and optical-fiber processing, the reaction chamber for plasma generating, and the reaction chamber for CVD etc.

[0060] Conventionally, in in a  $NH_4F-HF$  system electrolytic bath, nickel electrode is used as an electrode for  $NF_3$  composition. This reason is that the carbon particle produced for local destruction thru/or collapse of the carbon electrode under electrolysis operation, or gradual partial exfoliation reacts with a fluorine,  $CF_4$  mixes into  $NF_3$ , and there is a fault from which it becomes difficult [ separation ] very [ it ] since the difference of both boiling point is very small,

about 1 degree C and when general carbon material is used. However, by the conventional approach using nickel electrode, there is a fault that the current efficiency over NF<sub>3</sub> generating is very as bad as about 50%.

[0061] Since the local destruction or the gradual partial exfoliation which produce not only the destruction with the big carbon electrode of this invention but also a carbon particle do not occur to it, there is no risk of CF<sub>4</sub> generating. Therefore, when the carbon electrode of this invention is used, there is a big advantage that NF<sub>3</sub> of a high grade is obtained with high current efficiency. As an electrolytic bath for NH<sub>3</sub> manufacture, KF-NH<sub>4</sub> F-HF system fused salt and NH<sub>4</sub> F-HF system fused salt can be used advantageously. If a KF-NH<sub>4</sub> F-HF system electrolytic bath is used especially, current efficiency will become 70% or more. In the case of a NH<sub>4</sub> F-HF system electrolytic bath, use of the carbon electrode which performed sinking-in processing is desirable.

[0062] As stated above, the carbon electrode of this invention is not only excellent in the mechanical strength, but is chemically stable, and the intercalation compound generation by which knowledge was newly carried out to it being one cause of big destruction cannot break out easily in HF content molten salt electrolysis. The carbon electrode of this invention is useful, although electrolysis actuation of HF content fused salt is made to perform in the stable condition and a product with high purity is moreover manufactured.

[0063]

[Example] Next, although an example and the example of a comparison explain this invention to a detail further, this invention is not limited to an example.

[0064] The corks of the mosaic structure which is about 10 microns were ground below to 325 meshes (Tyler), and it considered as the aggregate, and the average size of an example 1 and an example of comparison 1 optical-anisotropy field (mosaic section) added the coal-tar pitch as a binder at a rate of 90 weight sections to the aggregate corks 100 weight section, carried out kneading under 180-220-degree C heating, ground mixture below to 100 meshes (Tyler), and considered as molding powder. Molding powder was fabricated with metal mold in the 125x250x75mm rectangular parallelepiped with the moulding pressure of 800kg/cm<sup>2</sup>, this was calcinated at 1000 degrees C with the programming rate in 2 degrees C/hr, and the carbon material was obtained (example 1).

[0065] Except having changed the amount of the coal-tar pitch as a binder into 50 weight sections, the carbon material obtained like the example 1 was heat-treated and graphitized at 2800 more degrees C, and the graphitization ingredient was obtained (example 1 of a comparison).

[0066] Ten 10x10x60mm samples were started from the two above-mentioned sorts of samples, respectively. When the three-point bending test (a sample is supported on the two supporting points and a load is placed upside down in the center between the supporting points) was presented with this in the distance between the supporting points of 40mm, the average flexural strength was as follows.

Example 1 Example 1 of 57MPa comparison 46MPa [0067] Moreover, the 5x30x1mm sample was started from the two above-mentioned sorts of samples, respectively, this was made into the anode plate, the potential scan was carried out with the potential scan speed of 5 mV/sec in 25-degree C 18M concentrated sulfuric acid by having used the 2nd mercury of a sulfuric acid as the reference electrode, having used Pt plate as cathode, and it asked for the single-sweep-operation voltamogram.

[0068] That for which it asked about the sample of an example 1 was shown in drawing 1. Current density became max, the summit potential corresponding to intercalation compound generation of the 1st stage was observed by 1.4V, and collapse of an electrode was not seen even if it repeated the potential scan 50 times in 0-1.5V.

[0069] On the other hand, by the sample which the example 1 of a comparison graphitized, like, current density became max, the summit potential corresponding to generation of the intercalation compound of the 1st stage shown in drawing 2 was observed by 0.9V, and, moreover, the electrode collapsed at the time of 1.05V of a time [ 1st ] potential scan.

[0070] The 250x70x15mm sample was started from two sorts of carbon material obtained in the

example 2, example of comparison 2 example 1, and the example 1 of a comparison, and electrolysis with constant current was performed by 7 A/dm<sup>2</sup>, keeping it strict in cathode at the electrolytic bath temperature of 90 degrees C, and bath presentation KF and 2HF using iron with the cell of 50A scale by making this into an anode plate.

[0071] The electrode of the example 1 of a comparison was destroyed in 14 days by part for a joint with the terminal for the energization to an anode plate. Moreover, when CF<sub>4</sub> concentration contained in generation fluorine gas was measured, it was 500 ppm or more on the average (example 2 of a comparison).

[0072] On the other hand, CF<sub>4</sub> content was also always kept at 20 ppm or less, without the electrode of an example 1 breaking three months or more (example 2).

[0073] The 250x70x15mm sample was started from the carbon material created like example 3 example 1, and the cell of 50A scale performed electrolysis with constant current of 5 A/dm<sup>2</sup> in cathode at the electrolytic bath temperature of 120–150 degrees C using the electrolytic bath of bath presentation KF and 2 HF+NH<sub>4</sub>F using iron by making this into an anode plate. [0074] Current efficiency was very high compared with 70% and the method of using the conventional nickel anode. Moreover, the amount of CF<sub>4</sub> under generation NF<sub>3</sub> is 500 ppm or less, and this means that NF<sub>3</sub> with very high purity was obtained compared with the chemistry method (CF<sub>4</sub> : generally 1000 ppm or more) generally conventionally used instead of the electrolytic decomposition process by the badness, therefore the nickel electrode of electrolysis effectiveness.

[0075] The temporary-quenching corks (temporary-quenching temperature: 1200–1300 degrees C) of the mosaic structure which is about 10 microns were ground below to 325 meshes (Tyler), and it considered as the aggregate, and the average size of an example 4 optical-anisotropy field (mosaic section) added the coal-tar pitch as a binder at a rate of 90 weight sections to the aggregate corks 100 weight section, carried out kneading under 180–220-degree C heating, ground mixture below to 100 meshes (Tyler), and considered as molding powder. Molding powder was fabricated with metal mold in the 125x250x75mm rectangular parallelepiped with the moulding pressure of 800kg/cm<sup>2</sup>, calcinated this at 1000 degrees C with the programming rate in 2 degrees C/hr, and obtained the carbon material.

[0076] Ten 10x10x60mm samples were started from the above-mentioned sample. When the three-point bending test was presented with this like the example 1, the average flexural strength was as follows.

Example 4 100MPa [0077] Moreover, the 5x30x1mm sample was started from the above-mentioned sample, this was made into the anode plate, the potential scan was carried out with the potential scan speed of 5 mV/sec in 25-degree C 18M concentrated sulfuric acid by having used the 2nd mercury of a sulfuric acid as the reference electrode, having used Pt plate as cathode, and it asked for the single-sweep-operation voltamogram. Consequently, current density became max, the summit potential corresponding to intercalation compound generation of the 1st stage was observed by 1.4V, and destruction of an electrode was not seen even if it repeated the potential scan 50 times in 0–1.5V.

[0078] The 250x70x15mm sample was started from the carbon material obtained in the example 5 example 4, and electrolysis with constant current was performed by 7 A/dm<sup>2</sup>, keeping it strict in cathode at the electrolytic bath temperature of 90 degrees C, and bath presentation KF and 2HF using iron with the cell of 50A scale by making this into an anode plate. Consequently, CF<sub>4</sub> content was also always kept at 10 ppm or less, without this electrode breaking three months or more.

[0079] The 250x70x15mm sample was started from the carbon material obtained in the example 6 example 4. The average aperture of pore of the porosity of these samples was 1 micrometer or less at 7 – 8%. :LiF, LiF+NaF (mole ratio 1:1) and CsF+NaF (mole ratio 1:1) which performed sinking-in processing for these samples using the following metal fluoride systems per each, AlF<sub>3</sub>+NaF (mole ratio 3:1), MgF<sub>2</sub> and CaF<sub>2</sub>, NiF<sub>2</sub>+NaF (mole ratio 2:1). Sinking-in processing carried out contact coexistence of the sample under a molten-metal fluoride (or mixture) and pressurization, after heating the metal fluoride (or mixture) to the melting temperature, and it was performed by introducing into pore.

[0080] The porosity of a sample became zero after sinking-in processing, and what the above-mentioned metal fluoride (or mixture) sinks in completely into pore (filling factor: 100%) became clear. Moreover, flexural strength rose rather, without 103MPa(s) and degradation on the strength by sinking in also producing flexural strength.

[0081] Electrolysis with constant current was performed by current density 7 A/dm<sup>2</sup>, keeping it strict in cathode at the electrolytic bath temperature of 90 degrees C, and bath presentation KF-2HF using iron with the cell of 50A scale by making into an anode plate the metal fluoride (or mixture) sinking-in electrode prepared in the example 7 example 6. Consequently, this electrode had 0.5 – 1V bath voltage lower than the non-sunk in electrode, and electrolysis continued it stably over three months or more. Moreover, CF<sub>4</sub> content in a generation fluorine was also always kept at 10 ppm or less.

[0082]

[Effect of the Invention] So that clearly also from the above-mentioned example The carbon electrode of this invention with which are satisfied of two conditions that flexural strength is 50 or more MPas, and the potential in which the current peak corresponding to the 1st stage intercalation compound generation of the voltamogram for which it asked with the potential sweep method in the inside of concentrated sulfuric acid appears is more than 1.2V (mercury electrode criteria) Neither destruction nor collapse nor exfoliation is caused during electrolysis, therefore the product of mixing of electrolysis operation not only being carried out but a request, for example, the amount of CF<sub>4</sub> to the inside of fluorine gas, is very low to stability over a long period of time, and it is very useful as an electrode for HF content molten salt electrolysis.

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[Translation done.]

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2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] It is drawing having shown the single-sweep-operation voltamogram for which it asked by the potential scan of potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid about the carbon electrode by this invention of an example 1.

[Drawing 2] It is drawing having shown the single-sweep-operation voltamogram for which it asked by the potential scan of potential scan speed 5 mV/sec in 25-degree-C concentrated sulfuric acid about the carbon electrode of the example 1 of a comparison.

[Drawing 3] It is the outline sectional view of the electrolytic device of this invention showing the interior [ like ] 1 voice.

[Drawing 4] It is the outline sectional view which met the IV-IV line of drawing 3 .

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[Translation done.]

\* NOTICES \*

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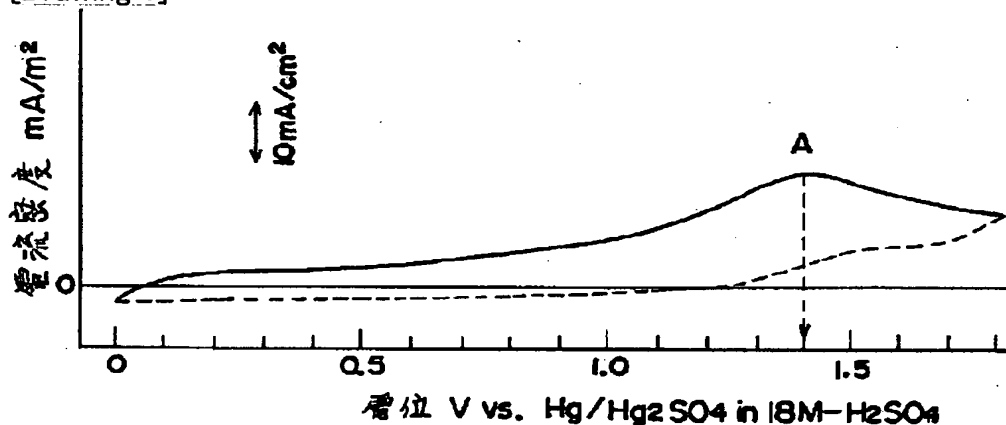
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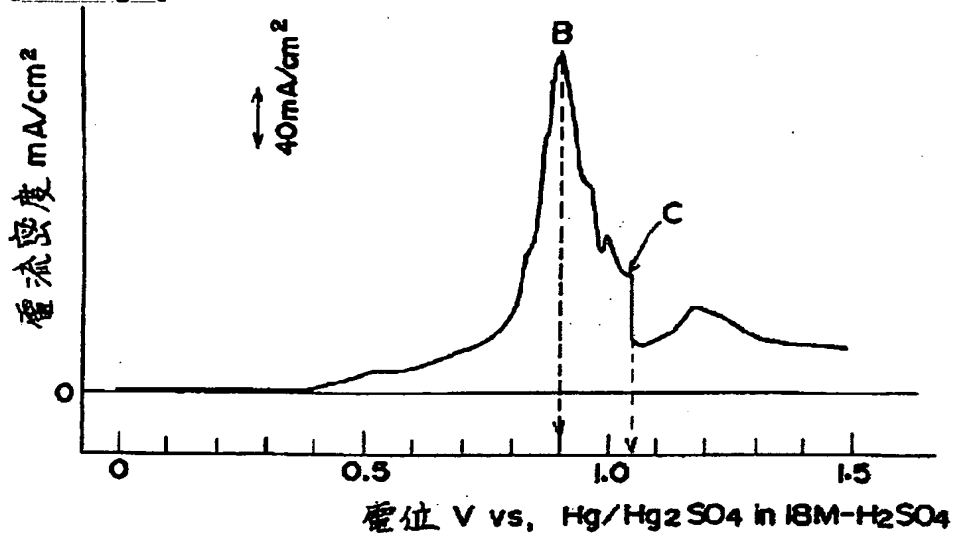
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DRAWINGS

[Drawing 1]

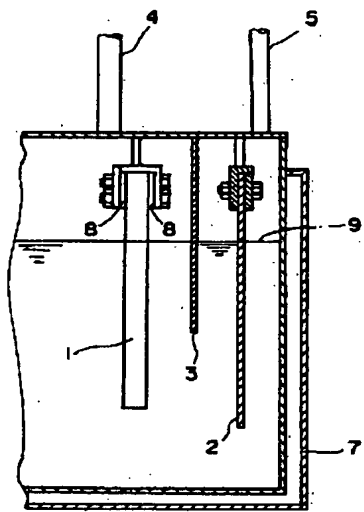


[Drawing 2]

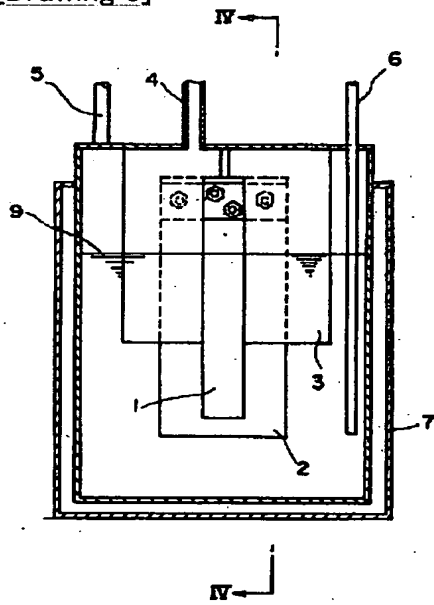


[Drawing 4]





[Drawing 3]



[Translation done.]

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1/24	A	8414-4K		
11/03		8414-4K		

審査請求 未請求 請求項の数 4(全 10 頁)

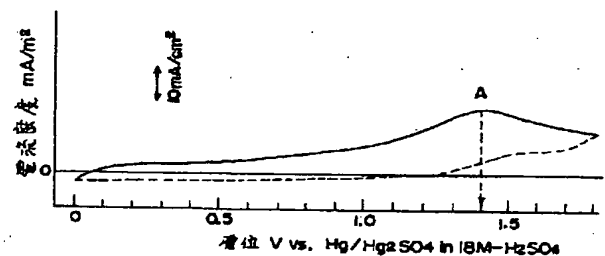
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(54)【発明の名称】 炭素電極ならびにそれを用いるHF含有溶融塩の電解方法及び装置

(57)【要約】

【目的】 HF含有溶融塩の電解に陽極として用いた際に、電解装置における陽極への通電用端子部との接合部分における破壊の危険(層間化合物の生成による)及び局所的な破壊と緩徐な部分的剥落の危険(機械的強度の不足による)のない炭素電極を提供することを目的とする。

【構成】 多孔性炭素ブロックよりなり、曲げ強度が50MPa以上であり、且つ、25℃濃硫酸中における電位走査速度5mV/secの電位走査により求めた単掃引ボルタモグラムにおいて最大の電流密度を有するピークを硫酸第二水銀を基準電極として1.2V以上の電位に示す。



## 【特許請求の範囲】

【請求項1】 多孔性炭素ブロックよりなり、曲げ強度が50MPa以上であり、且つ、25℃濃硫酸中における電位走査速度5mV/secの電位走査により求めた単掃引ボルタモグラムにおいて最大の電流密度を有するピークを硫酸第二水銀を基準電極として1.2V以上の電位に示す炭素電極。

【請求項2】 該炭素ブロックが、LiF、NaF、CsF、AlF<sub>3</sub>、MgF<sub>2</sub>、CaF<sub>2</sub>、NiF<sub>2</sub>から選ばれた少なくとも1種の金属フッ化物を気孔中に有することを特徴とする請求項1記載の炭素電極。

【請求項3】 HF含有溶融塩よりなる電解浴を、請求項1又は2記載の炭素電極を陽極として電解することと特徴とするHF含有溶融塩の電解方法にあって、該HF含有溶融塩がKF-HF系、CsF-HF系、NOF-HF系、KF-NH<sub>4</sub>F-HF系又はNH<sub>4</sub>F-HF系である電解方法。

【請求項4】 電解槽及び陽極と陰極を包含するHF含有溶融塩の電解装置にあって、該陽極が請求項1又は2記載の炭素電極であることを特徴とする電解装置。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は炭素電極ならびにそれを用いるHF含有溶融塩の電解方法及び電解装置に関する。更に詳しくは、機械的強度に優れているのみならず化学的に安定で、HFを同伴するフッ素雰囲気に曝露されるHF含有溶融塩電解において、割れの1つの原因であると新しく知見された層間化合物生成が起き難く、電解操作を安定な状態で行なわしめ、しかも純度の高い製品を製造するのに有用な炭素電極に関する。本発明はまた、上記の炭素電極を陽極として用いることを特徴とするHF含有溶融塩の電解方法及び装置に関する。

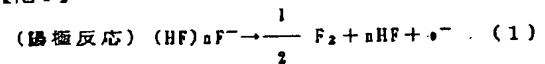
## 【0002】

【従来の技術および発明が解決しようとする問題点】 HF含有溶融塩の電解方法の代表的な例としてフッ素の電解製造が挙げられる。フッ素の製造法としては、現在、約90℃のフッ化カリウムとフッ化水素の混合溶融塩中で電気分解を行なう中温法が一般に採用されている。

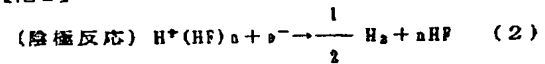
【0003】 中温法における浴組成はKF・2HFであり、これが広く用いられる理由は、融点付近でHFの蒸気圧が低く、しかも浴中のHF濃度の変動によっても浴の融点に変化しにくいことにある。電解槽の陽極としては、金属は陽極溶解によって使用できないため専ら炭素が電極材として用いられている。陰極としては、研究レベルでは、鉄、スチール、ニッケル、モネル等が用いられるが、工業的には、入手容易性と経済性から鉄が使用され、通常、電流密度7～13A/dm<sup>2</sup>、浴電圧8.5～15Vで電解が行なわれる。

【0004】 この電解方法における陽極および陰極での電極反応は次のように表わされる。

## 【化1】



## 【化2】



このようなフッ素の電解製造において用いられる炭素電極には次のような困難な問題が伴うことが知られている。

【0005】 (イ) 電解装置における陽極への通電用端子部は通常銅製のボルトとナットにより炭素電極の一端を接合固定しているが、電解中にこの部分で炭素電極の大きな破壊が起こる。

【0006】 (ロ) 多孔質の炭素電極は一般に機械的強度が少なく、電解中に、上記の陽極への通電用端子部への固定部分以外の場所でも局部的な崩壊や緩徐な部分的剥落が発生し、微細な炭素粉を生じ（ここにおいて、「緩徐な部分的剥落」とは炭素電極が表面よりの炭素粒子の脱落の形で徐々に損壊していくことを意味する）、これがフッ素と容易に反応してCF<sub>4</sub>となり、製品としてのフッ素中に混入する。

【0007】 (ハ) 電解中に炭素陽極上で生ずるF<sub>2</sub>と炭素陽極の反応により、表面エネルギーが極めて低いフッ化グラファイトが生成する。炭素陽極上のフッ化グラファイトが生成した部分では浴との濡れが悪くなり電気化学的に不活性となる。電極の有効面積はフッ化グラファイトによる電極表面の被覆率の増大によって減少し、真の電流密度は増大する。これがフッ素電解における陽極過電圧の主要な原因であり、フッ化グラファイトによる被覆率が20%を越えると電圧の急上昇が観察され通電不能となる。この現象は陽極効果と呼ばれ、HF含有溶融塩の工業的電解法において大きな問題となっている。

【0008】 これらの問題点のうち、(ハ) の陽極効果については、本発明者らはすでに炭素ブロックの気孔中にフッ化リチウムを含む金属フッ化物を効果的に含浸することにより抑制し得ることに成功している（特開平2-47297号）。

【0009】 しかし、上記した(イ)及び(ロ)の問題（即ち炭素電極の固定部分での大きな破壊及び局部的崩壊と緩徐な部分的剥落）は未だ解決されておらず、HF含有溶融塩の実際の電解操作において致命的なことである。従って、長時間に亘って安定したHF含有溶融塩の電解を可能にし、又高純度の製品を得るために、これらの破壊及び崩壊と剥落の危険の無い炭素電極の開発が切に望まれていた。

## 【0010】

【問題を解決するための手段および作用】 炭素電極は一般に、石油コークス、ピッチコークスを粉碎して骨材と

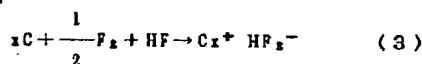
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し、これに結合材としてコールタールピッチや合成樹脂を加えて混捏、成形、焼成して得られる多孔性炭素ブロックよりなるものである。この際用いられる骨材コークスは黒鉛結晶子が多少ともある方向に整列した領域を持っており、これが、熱処理温度が高くなると共に成長、発達する。

【0011】研究の結果、本発明者らは、曲げ強度に代表される機械的強度の不足が炭素電極の局所的な破壊と緩徐な部分的剥落をもたらすほかに、電解時の炭素電極の上記した黒鉛構造領域の化学的挙動が、HF含有溶融塩の電解操作の際に、電解浴の上部に離れて位置する陽極への通電用端子部に接合固定された炭素電極部分の破壊につながることを知見した。

【0012】即ち、本発明者らは、炭素電極がHFを同伴したF<sub>2</sub>雰囲気中に曝されると、(3)式に示される反応によって層間化合物が生じ、層間化合物の生成に伴って、配列している黒鉛層間が押し抜けられ、層間隔が大きくなる結果炭素材が著しく膨張して破壊に至ることを見出した。

【化3】



【0013】本発明者らは、この層間化合物の生成による炭素電極の大きな破壊の問題、及び電解中の炭素電極の局所的な破壊もしくは崩壊と緩徐な部分的剥落を無くすために、鋭意研究の結果、特定レベル以上の曲げ強度を有し、且つ、特定条件下での電位走査によって求められた単掃引ボルタモグラムにおいて特定レベル以上の電位にピークを示すという2つの要件を満たす炭素電極が従来の炭素電極に付随する上記の問題を解決でき、HF含有溶融塩の電解の安定な操業及び高純度製品の製造に陽極として有利に使用できることを意外にも知見し、本発明に到達したものである。

【0014】従って、本発明の第1の目的は、HF含有溶融塩の電解に陽極として用いた際に、電解装置における陽極への通電用端子部との接合部分における破壊の危険及び局所的な破壊と緩徐な部分的剥落の危険のない炭素電極を提供することである。

【0015】また、本発明の第2の目的は、安定な電解操業が可能で高純度製品を得ることのできる、上記の炭素電極を陽極として用いるHF含有溶融塩の電解方法を提供することである。

【0016】また、本発明の第3の目的は、上記の炭素電極を陽極として用いることによって、陽極としての炭素電極を交換する必要なく長時間の電解を可能にするHF含有溶融塩の電解装置を提供することである。

【0017】本発明の上記及びその他の諸目的、諸特徴、諸利益は添付の図面と以下の詳細な説明及び前記の特許請求の範囲から明らかとなる。

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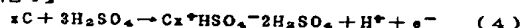
【0018】即ち、本発明によれば、多孔性炭素ブロックよりなり、曲げ強度が50MPa以上であり、且つ、25℃濃硫酸中における電位走査速度5mV/secの電位走査により求めた単掃引ボルタモグラムにおいて最大の電流密度を有するピークを硫酸第二水銀を基準電極として1.2V以上の電位に示す炭素電極が提供される。

【0019】以下、本発明の炭素電極の特徴を説明する。炭素材における黒鉛結晶の成長は、炭素粒子を超えて、また黒鉛結晶子の配向した領域を囲む非晶質部分を超えては起こり難い。それ故、骨材コークスを数ミクロンないしは数十ミクロンにまで微粉砕し、これに比較的多量のピッチバインダーを加えて炭素材を作れば、組織中の黒鉛結晶子の配向を抑制することができること、及び、細かいモザイク組織のコークスを骨材に使用するか、または、数ミクロンの粒径のメソフェーズマイクロビーズのような微粒子原料を使用することで黒鉛結晶の成長を制限することができ、黒鉛結晶の成長が制限された炭素ブロックは、上記(3)式で示した層間化合物の生成反応は起こり難いことを知見した。もちろん、炭素ブロックを生成するための焼成のための熱処理温度は、黒鉛結晶の成長を促さないように可及的に低い温度で行なわれることが望ましい。

【0020】炭素ブロックについての層間化合物生成の難易性は、濃硫酸中において求めた単掃引ボルタモグラム(linear sweep voltammogram)において、該炭素ブロックが最大の電流密度を有するピークを示す電位(基準電極としては硫酸第二水銀電極を使用する)より判断することができる。尚、上記のピークは、炭素と硫酸との第1ステージ層間化合物生成反応に対応する。

【0021】濃硫酸中での炭素材の黒鉛層間化合物生成反応は次の(4)式により示される。

【化4】



【0022】(4)式の反応によって層間化合物が生じる際には黒鉛層間は押し抜けられねばならず、単掃引ボルタモグラムを求めるための電位走査を行なっている間に層間侵入物質として濃硫酸が黒鉛層間に拡散する。黒鉛結晶子の発達が悪いと上記の黒鉛層間の拡大と層間侵入物質の拡散という過程に対する活性化エネルギーが大きくなり、黒鉛層間化合物を生成するための電位が黒鉛結晶子の良く発達したものに比して貴になる。即ち、単掃引ボルタモグラムにおいて最大の電流密度を有するピーク(該ピークは炭素と硫酸との第1ステージ層間化合物生成に対応する)の表われる電位が貴なほど、その炭素電極は層間化合物を作り難い。

【0023】本発明の電極においては、25℃濃硫酸中における電位走査速度5mV/secでの電位走査により求めた単掃引ボルタモグラムにおいて、最大の電流密度を有するピークを硫酸第二水銀を基準電極として1.2V以上の電位に示すことが必須である(炭素電極が該ピークを示

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す電位をこれより屢々「ピーク電位」と略記する)。上記のように、このピークは炭素と硫酸との第1ステージ層間化合物の生成に対応する。第1ステージ層間化合物の生成の確認は、該ピークに達した時点で電位走査を止め、炭素電極をX線回折にて調べることにより行なうことができる。このピーク電位が1.2V以上である要件を満足することによりはじめて、電解操業中に層間化合物の生成による膨張に起因する炭素電極の比較的大きな破壊〔即ち、前記(イ)の問題〕を無くすることができる。ピーク電位は好ましくは1.3V以上である。

【0024】また、前記(ロ)に述べた電解中の炭素電極の機械的強度の不足による局所的な破壊もしくは崩壊及び緩徐な部分的剥落は、電解浴中に微小な炭素片や炭素粉を浮遊させることになり、これが活性であると共に大きい表面積を持つため容易にF<sub>2</sub>ガスと反応してガス状のCF<sub>4</sub>を生成し、所望製品、例えばF<sub>2</sub>中に混入することになる。これを防止するには炭素電極を構成する炭素材が機械的に高強度のものであることが必要である。従って、本発明の炭素電極は50MPa以上の曲げ強度を有することが必須である。本発明の炭素電極の曲げ強度は、好ましくは55MPa以上、さらに好ましくは80MPa以上である。

【0025】上記の2つの必須要件を満足する炭素材を得るためには、例えば、微粉状骨材コークスにほぼ等重量又はそれ以上のピッチバインダーを加え結合の役割を分担するバインダーコークスの量を増大させるようにするか、又は微小モザイク組織のコークスや生コークスのように熱処理段階で大きい収縮を示す骨材を用い炭素材の緻密化をはかるか、あるいは変質ピッチやメソフェーズマイクロビーズのような骨材と結合材が一体的に構成された一元系材料を用いることにより達成することができる。

【0026】ここで言う微小モザイク組織とは、ピッチを加熱してメソフェーズ小球体が生成する過程でそのサイズが10μm以下のものがモザイク様に等方性マトリックス中に一様に分散しているものをいう。このような構造をもつ炭素材を加熱するとモザイク部分は大きく収縮して高密度材料が得られる。

【0027】また、上記のように、ピッチから生成したメソフェーズ小球体を分離して得られるいわゆるメソフェーズマイクロビーズはそのまま一元系材料として本発明の炭素電極の原料として有利に用いることができる。

【0028】ピッチを乾留する際に雰囲気制御を行なうと空気中では非黒鉛化炭素材、窒素ガス中では易黒鉛化炭素材の前駆体が得られ、これらを変質ピッチと言い、やはり、一元系材料として本発明の炭素電極の製造に用いることができるものである。

【0029】即ち、本発明の炭素電極は、例えば、粒径が3~20μmの微粉状の仮焼した骨材コークス100重量部

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にコールタールピッチ、石油ピッチのようなピッチバインダー約80~130重量部を配合した2元系材料、又は変質ピッチやメソフェーズマイクロビーズのような1元系材料を熱処理して得られる炭素材をブロック状に切出すなどの方法により製造することができる。熱処理温度は、望まれる機械的強度及び電解中の層間化合物の生成防止の目的からも、通常1000℃~1500℃、好ましくは1000℃~1200℃である。このようにして得られた炭素ブロックは多孔性であるが、従来の炭素電極に較べて緻密な構造を有している。すなわち、気孔率は約2%から約10%で、気孔の平均口径は非常に小さく、例えば、約1μm程度である。

【0030】本発明の炭素電極の炭素材の機械的特性は、その曲げ強度を以て表示することができる。本発明の炭素電極の曲げ強度は、JIS R7222の方法に従って支点間距離40~80mm3点曲げテスト(サンプルを2つの支点で支持し、支点間の中央で下向きに荷重する)で測定した時50MPa以上を示すことが必須である。曲げ強度は、好ましくは55MPa以上、さらに好ましくは80MPa以上である。このような曲げ強度を有する炭素電極をHF含有溶融塩電解(例えば、フッ素製造のためのKF-2HFなどのKF-HF系溶融塩の電解)の陽極に用いるとき、CF<sub>4</sub>の発生を痕跡程度に抑えることができる。

【0031】上記したように、本発明の炭素電極は、50MPa以上の曲げ強度を示し、かつ、25℃濃硫酸中における電位走査速度5mV/secでの電位走査により求めた単掃引ボルタモグラムにおいて最大の電流密度を有するピークを硫酸第2水銀を基準電極として1.2V以上の電位に示すという2つの条件を満足することが必須の要件である。この2つの条件の両者を満足することによってはじめて、HF含有溶融塩の電解において、陽極への通電用端子部との接合部における大きな割れの発生及び局所的な破壊乃至崩壊と緩徐な部分的剥落の発生の両方を著しく減少させることができ、安定な電解操業と高純度製品の製造を可能にするのであり、この2要件の1つでも満足しなければ本発明の目的を達成することはできない。

【0032】本発明の好ましい態様においては、前記の陽極効果抑制のため、炭素電極はさらに多孔性炭素ブロックの気孔に含有された少なくとも1種の金属フッ化物を有する。好適な金属フッ化物としては、LiF、NaF、CsF、AlF<sub>3</sub>、MgF<sub>2</sub>、CaF<sub>2</sub>、NiF<sub>2</sub>などを挙げることができる。これらの金属フッ化物は高温高圧の条件下で、炭素ブロックの気孔中に単独でも導入することができる。しかし、炭素ブロックの気孔への導入を容易且つ効果的に行なう観点から、金属フッ化物の導入は複数種の金属フッ化物の混合物の形で行なうのが好ましい。その理由は、溶融した金属フッ化物混合物の表面張力は、溶融した個々の金属フッ化物の表面張力よりも小さいからである。金属フッ化物の特に好ましい組合

せとして、 $AlF_3$ と $NaF$ の組合せ及び $LiF$ と $NaF$ の組合せを挙げることができる。モル比は特に限定されないが、一般に、 $AlF_3/NaF$ 系で約3/1から約3/2、また、 $LiF/NaF$ 系で約0.5/1から約2/1がそれぞれ好ましい。 $NaF$ を他の金属フッ化物と組み合わせて用いるのが好ましいのは、 $NaF$ はフッ化第二鉄（これは電解装置の鉄製器具からの鉄の溶出によって生成し、電解浴に粘性を与えるため好ましくない）と容易に反応して錯体( $NaFeF_3$ )を形成して沈殿させることにより第二鉄イオンの望ましくない影響を除去できるからである。

【0033】炭素ブロックに少なくとも1種の金属フッ化物を含浸させると、金属フッ化物は炭素ブロックの微細な気孔中に含まれる。少なくとも1種の金属フッ化物を含浸させた炭素ブロックは曲げ強度が大幅に向上することを、意外にも知見した。

【0034】炭素ブロックの気孔中に金属フッ化物（又は混合物）を充填させる方法は、炭素ブロックの気孔中への充填率が少なくとも30%、好ましくは少なくとも50%、更に好ましくは65%以上になるように充填することが

【0035】例えば、金属フッ化物（又は混合物）をその融点以上に加熱し、熔融状態で炭素ブロックと接触共存させ、接触共存系に所定の圧力をかけて気孔中に熔融金属フッ化物（又は混合物）を導入したのち、所定の温度、通常は室温にまで炭素ブロックを冷却する方法によれば、金属フッ化物（又は混合物）を炭素ブロックの気孔中に容易に含浸圧入させることができる。この際、接触共存系にかかる圧力を制御することにより、炭素ブロックの気孔中の金属フッ化物（又は混合物）の充

【0036】上記の方法を更に具体的に説明する。例えば、 $AlF_3-NaF$ 系金属フッ化物混合物を $AlF_3/NaF$ のモル比が3:1となるように調製する。この混合物をルツボの中で、例えば、970~1050℃に加熱して充分熔融させた後、その中に炭素ブロックを入れ（炭素ブロックは金属フッ化物混合物を加熱熔融する前にルツボに入れておいてもよい）、炭素材の押圧手段を用いて混合熔融体中に浸漬するようにして固定する。このルツボを圧力容器に入れる。つぎに該容器内部を窒素ガス又はアルゴンガスで置換した後、約5~10℃/minの割合で約1000℃まで昇温し、次に該容器を10~50mmHgまで減圧する。この減圧操作は炭素ブロックの中の気孔より空気を除去して含浸圧入操作を容易にすると共に該材料の酸化を防止するものである。つぎに、このようにして熔融した金属フッ化物混合物と炭素ブロックとが接触共存した状態で、該容器内に不活性ガス、例えば窒素またはアルゴンを導入して、内圧を50から100kg/cm<sup>2</sup>で約30分~約2時間保持する。この後、該炭素ブロックを圧力容器から取り出し、大気中にて自然放冷す

れば、 $AlF_3-NaF$ 系の金属フッ化物混合物が気孔中に含まれた炭素ブロックよりなる、好ましい態様の本発明の炭素電極を得ることができる。

【0037】金属フッ化物（又は混合物）の充填率(X)は、炭素ブロック中の気孔の量を100%とすると、その気孔が金属フッ化物（又は混合物）で充填されている割合(%)を意味し、母材の炭素ブロックのかさ比重をA、真比重をA'、気孔率をPとし、又、金属フッ化物（又は混合物）充填電極の比重をBとすると、式 $B = A + XP$ により求められる。気孔率は水銀ポロシメーターにより測定することができる。

【0038】本発明の炭素電極を用いることにより、HF含有熔融塩の電解を安定に行なうことができる。

【0039】従って、本発明によれば更に、HF含有熔融塩よりなる電解浴を、上記の炭素電極を陽極として電解することを特徴とするHF含有熔融塩の電解方法にあって、該HF含有熔融塩がKF-HF系、CsF-HF系、NOF-HF系、KF-NH<sub>4</sub>F-HF系又はNH<sub>4</sub>F-HF系である電解方法が提供される。

【0040】本発明の方法においては、HF含有熔融塩がKF-HF系（好ましくはKF-2HF塩）、CsF-HF系又はNOF-HF系（好ましくはNOF-3HF塩）である場合、得られる電解製品はフッ素であり、HF含有熔融塩がKF-NH<sub>4</sub>F-HF系又はNH<sub>4</sub>F-HF系である場合、得られる電解製品は三フッ化窒素である。本発明の方法によれば、HF含有熔融塩の電解を安定に行なうことができるのみならず、所望の電解製品を高純度で得ることができる。

【0041】また、本発明によれば更に、電解槽及び陽極と陰極を包含するHF含有熔融塩の電解装置にあって、該陽極が上記の炭素電極であることを特徴とする電解装置が提供される。本発明の電解方法及び電解装置における陰極の材料は、水素過電圧が低く且つフッ化物を作り難いものであれば特に限定されないが、入手容易性及び経済性の観点から、工業的には鉄製陰極が用いられる。

【0042】本発明の装置については、図3及び図4に参照しつつ後で更に詳しく説明する。

【0043】本発明の驚くべき効果を実証するために、以下の実験を行なった。一例として、325メッシュ(Tyler)以下に粉碎した仮焼石油コークス粉100重量部に対して90重量部のコールタールピッチを加え、約150~250℃、好ましくは約180~220℃における加熱下で長時間混捏すると共に揮発分を調整し、冷却後再度粉碎し〔100メッシュ(Tyler)以下〕で成形し、1000℃で焼成して炭素ブロックを作った〔サンプル(1)〕。

【0044】一方、325メッシュ(Tyler)以下に粉碎した上記と同じ骨材コークスに骨材コークス100重量部に対して50重量部のコールタールピッチを混合し、それ以外は上記と同じ手法で混捏、粉碎、成形を行ない、その後

2800℃で熱処理を行なって炭素ブロックを得た〔サンプル(11)〕。

【0045】サンプル(1)は57MPaの曲げ強さを示したが、サンプル(11)は46MPaであった。

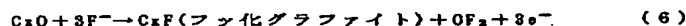
【0046】これらの炭素材について18M濃硫酸中25℃にて電位走査速度5mV/secで単掃引ボルタムメトリーを行なった。どちらの場合も、陰極には白金板、基準電極には濃硫酸中に浸漬させた硫酸第二水銀電極を用いた。

【0047】サンプル(1)及び(11)について得られた結果(即ち、単掃引ボルタモグラム)をそれぞれ図1及び図2に示した。図1より分かるように1000℃焼成材〔サンプル(1)〕では第1ステージ層間化合物生成ピーク(A)(ピーク電位)が1.4Vに観察された。又図2より分かるようにバインダー量が少なく且つ2800℃で熱処理した材料〔サンプル(11)〕では第1ステージ層間化合物生成ピーク(B)(ピーク電位)が0.9Vに観察された。

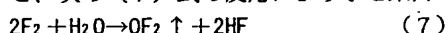
【0048】サンプル(1)(本発明)は電位を0から1.5Vの間で50回電位走査を続けても材料の破壊は見られなかったが、サンプル(11)(従来技術)では第1回20目の走査において1.05Vの時点(C)で炭素材の端から膨れあがり、濃硫酸液に浸漬されている部分が大きく膨張し\*



#### 【化6】



【0051】それ故、浴中の水を充分取り除くためにニッケル電極を用い低電流密度で電解してフッ素を発生させ、次の(7)式の反応により水を系外に取り除いた。



【0052】また、通電に際して、陽極への通電用端子部の金属と炭素電極の接触部分に可撓性黒鉛シートを挟み込み接触抵抗を低下させると同時に浴またはF<sub>2</sub>やHFのこの部分への侵入を防いだ。

【0053】上記のような準備操作の後以下のような電解操作を行なった。

【0054】サンプル(11)(焼成温度2800℃で調製した、曲げ強度が46MPaであり且つ前記条件下で求めた単掃引ボルタモグラムにおけるピーク電位が0.9Vである材料)を陽極とし7A/dm<sup>2</sup>で定電流電解したところ、14日間でKH・2FH浴に浸漬されている部分およびブスバーと炭素電極が接触している部分で破壊した。電解中、生成フッ素ガスに含まれるCF<sub>4</sub>をガスクロマトグラフィー法および赤外吸収スペクトル法にて測定したところ、常時500ppm以上であった。

【0055】一方、サンプル(1)(焼成温度1000℃で調製した、曲げ強度が57MPaであり且つ前記条件下で求めた単掃引ボルタモグラムにおけるピーク電位が1.4Vである材料)を陽極とし7A/dm<sup>2</sup>で定電流電解したところ、70日間電極の破壊はなかった。また、フッ素ガス中のCF<sub>4</sub>も平均20ppmと極めて低かった。

\*てしまつて電極が破壊した。

【0049】次に、調製した上記二種類の炭素材を電極として用いて、フッ素製造のための電解浴中で定電流法により電解を行ない電極の性能評価を行なった。即ち、電解浴にはKF・2HF浴を用いて陽極には調製した炭素材(250×70×15mm)、陰極には鉄板(160×100mm、2枚)を用いた。電解中、浴は90℃に保ち、無水フッ酸を適宜浴に吹き込み浴組成をKF・2HFの一定値に保った。

【0050】電解の際、安定な操業を行なうためには、浴の充分な脱水を行なうことと、陽極への通電用端子部のアッセンブリーを工夫してF<sub>2</sub>やHFまたは浴の該端子部分への侵入を防止することが重要である。浴中に水があると炭素と水の放電生成物である酸素が反応して酸化グラファイトを生ずる。酸化グラファイトは不安定な物質で電極で生じたフッ素原子と容易に反応し安定なフッ化グラファイトとなる。このためわずかな水(500ppm位でも)が浴中に存在しても、通電するとフッ化グラファイトを生じやすくなり、これの被覆率の増加にしたがって電気化学的に不活性な部位が増加して真の電流密度が上昇し、その結果として陽極過電圧が増大する。これらの反応を(5)および(6)式に示す。

#### 【化5】



【0056】このように、本発明の電極は割れに対する耐性が著しく高く安定な電解操業を可能にすると同時に、CF<sub>4</sub>の混入の無い高純度フッ素を目的としたフッ素の電解製造用電極として極めて有用なものである。

【0057】以上述べたように、本発明により、曲げ強度が50MPa以上であり且つ前記条件下で求めた単掃引ボルタモグラムにおいてピーク電位が1.2V以上であるという2つの条件の両者を満足する炭素材を陽極として用いてKF・2HF電解浴中にてフッ素を電解製造するとフッ素中へのCF<sub>4</sub>の混入量を抑制でき、しかも電極が割れや破壊をおこすことなく長時間電解を行なうことができる。従って、本発明の炭素電極は、HF含有溶融塩の電解において大きな利点を有している。

【0058】本発明の炭素電極は例えば図3及び図4に示すような電解装置に適用できる。図3は本発明の電解装置の一態様の内部を示す概略断面図であり、図4は図3のI-V-I線に沿った概略断面図である。図3及び図4において、1は本発明の陽極、2は陰極で例えば鉄を用いる。またF<sub>2</sub>とH<sub>2</sub>の混合を防止するために軟鋼又は軟鋼にモネルメタルを被覆したスカート(3)が設けられている。4はF<sub>2</sub>出口、5はH<sub>2</sub>出口、6(図3)はHF供給口、7は温水ジャケットで電解槽を80~90℃に保つために用いる。また、8(図4)は陽極への通電用端子部に挟み込んだ可撓性黒鉛シートで、浴やF<sub>2</sub>、HFのこの部分への侵入を防止すると共に応力緩和用パッキンとして

の機能および接触抵抗の増大防止の機能も発揮される。  
9は電解時のHF含有溶融塩電解浴の液面を示す。

【0059】又、本発明の炭素電極は $\text{NF}_3$ の電解合成用にも有利に適用でき、この場合、HF含有溶融塩は $\text{KF}-\text{NH}_4\text{F}-\text{HF}$ 系電解浴や $\text{NH}_4\text{F}-\text{HF}$ 系電解浴である。 $\text{NF}_3$ はドライエッチングガス、光ファイバー処理用ガス、プラズマ発生用反応室およびCVD用反応室の洗浄用ガスなどとして使用されている。

【0060】従来、 $\text{NF}_3$ 合成用電極としては、 $\text{NH}_4\text{F}-\text{HF}$ 系電解浴中の場合にはNi電極が用いられている。この理由は、一般の炭素材を用いると、電解操作中の炭素電極の局部的破壊乃至崩壊や緩徐な部分的剥落のために生じた炭素粒子がフッ素と反応して $\text{CF}_4$ が $\text{NF}_3$ 中に混入し、両者の沸点の差が約 $1^\circ\text{C}$ と極めて小さいため分離が極めて困難となる欠点があるからである。ところがNi電極を用いる従来の方法では、 $\text{NF}_3$ 発生に対する電流効率が50%程度と極めて悪いという欠点がある。

【0061】それに対し、本発明の炭素電極は、大きな破壊はもとより、炭素粒子を生じる局部的破壊や緩徐な部分的剥落が発生しないため $\text{CF}_4$ 発生の危険が無い。従って、本発明の炭素電極を用いると高純度の $\text{NF}_3$ が高電流効率で得られるという大きな利点がある。 $\text{NH}_3$ 製造用の電解浴としては、 $\text{KF}-\text{NH}_4\text{F}-\text{HF}$ 系溶融塩や $\text{NH}_4\text{F}-\text{HF}$ 系溶融塩を有利に用いることができる。特に $\text{KF}-\text{NH}_4\text{F}-\text{HF}$ 系電解浴を用いると、電流効率は70%以上となる。 $\text{NH}_4\text{F}-\text{HF}$ 系電解浴の場合、含浸処理を施した炭素電極の使用が好ましい。

【0062】以上述べたように、本発明の炭素電極は機械的強度に優れているのみならず化学的に安定で、HF含有溶融塩電解において、大きな破壊の1つの原因であると新しく知見された層間化合物生成が起き難い。本発明の炭素電極はHF含有溶融塩の電解操作を安定な状態で行なわしめ、しかも純度の高い製品を製造するのに有用である。

#### 【0063】

【実施例】次に実施例及び比較例により本発明を更に詳細に説明するが、本発明は実施例に限定されるものではない。

#### 【0064】実施例1および比較例1

光学的異方性領域(モザイク部)の平均サイズが約10ミクロンのモザイク組織のコークスを325メッシュ(Tyler)以下に粉碎して骨材とし、骨材コークス100重量部に対してコールタールピッチを90重量部の割合でバインダーとして添加し、 $180\sim 220^\circ\text{C}$ の加熱下で混捏し、混合物を100メッシュ(Tyler)以下に粉碎して成形粉とした。成形粉は金型で $800\text{kg}/\text{cm}^2$ の成形圧で $125\times 250\times 75\text{mm}$ の直方体に成形し、これを $2^\circ\text{C}/\text{hr}$ での昇温速度で $1000^\circ\text{C}$ に焼成して炭素材料を得た(実施例1)。

【0065】バインダーとしてのコールタールピッチの量を50重量部に変えた以外は実施例1と同様にして得た

炭素材料をさらに $2800^\circ\text{C}$ に熱処理して黒鉛化し、黒鉛化材料を得た(比較例1)。

【0066】上記2種の試料からそれぞれ $10\times 10\times 60\text{mm}$ の試料10枚を切り出した。これを支点間距離40mmで3点曲げ試験(2つの支点上で試料を支持し、支点間の中央で下向きに荷重する)に供したところ、その平均曲げ強度は次の通りであった。

実施例1 57MPa

比較例1 46MPa

10 【0067】又、上記2種の試料からそれぞれ $5\times 30\times 1\text{mm}$ の試料を切り出し、これを陽極とし、Pt板を陰極、硫酸第2水銀を基準電極として、 $25^\circ\text{C}$ の18M濃硫酸中で $5\text{mV}/\text{sec}$ の電位走査速度で電位走査して単掃引ボルタモグラムを求めた。

【0068】実施例1の試料について求めたものを図1に示した。電流密度が最大となり第1ステージの層間化合物生成に対応するピーク電位は1.4Vに観察され、電位走査を $0\sim 1.5\text{V}$ の範囲で50回繰り返しても電極の崩壊は見られなかった。

20 【0069】これに対して比較例1の黒鉛化した試料では図2に示した様に、電流密度が最大となり第1ステージの層間化合物の生成に対応するピーク電位は0.9Vに観察され、しかも第1回の電位走査の1.05Vの時点で電極が崩壊した。

#### 【0070】実施例2および比較例2

実施例1及び比較例1で得た2種の炭素材から $250\times 70\times 15\text{mm}$ の試料を切り出し、これを陽極として50Aスケールの電解槽にて陰極には鉄を用い、電解浴温度 $90^\circ\text{C}$ 、浴組成 $\text{KF}\cdot 2\text{HF}$ に厳密に保ちながら $7\text{A}/\text{dm}^2$ で定電流電解を行なった。

30 【0071】比較例1の電極は14日間で陽極への通電用の端子との接合部分で破壊した。また生成フッ素ガス中に含まれる $\text{CF}_4$ 濃度を測定したところ平均して500ppm以上であった(比較例2)。

【0072】これに対して実施例1の電極は3ヶ月以上割れることなく、また $\text{CF}_4$ 含有量も常時20ppm以下に保たれた(実施例2)。

#### 【0073】実施例3

40 実施例1と同様にして作成した炭素材から $250\times 70\times 15\text{mm}$ の試料を切り出し、これを陽極として50Aスケールの電解槽にて陰極には鉄を用い、電解浴温度 $120\sim 150^\circ\text{C}$ で、浴組成 $\text{KF}\cdot 2\text{HF}+\text{NH}_4\text{F}$ の電解浴を用いて $5\text{A}/\text{dm}^2$ の定電流電解を行なった。

【0074】電流効率は70%と、従来のニッケル陽極を用いる方法に較べて極めて高かった。また、生成 $\text{NF}_3$ 中の $\text{CF}_4$ の量は500ppm以下で、これは電解効率の悪さ故にニッケル電極による電解法の代りに従来一般に用いられている化学法( $\text{CF}_4$ :一般に1000ppm以上)に較べて極めて純度の高い $\text{NF}_3$ が得られたことを意味している。

50 【0075】実施例4



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光学的異方性領域(モザイク部)の平均サイズが約10ミクロンのモザイク組織の仮焼コークス(仮焼温度: 1200~1300℃)を325メッシュ(Tyler)以下に粉碎して骨材とし、骨材コークス100重量部に対してコールタールピッチを90重量部の割合でバインダーとして添加し、180~220℃の加熱下で混捏し、混合物を100メッシュ(Tyler)以下に粉碎して成形粉とした。成形粉は金型で800kg/cm<sup>2</sup>の成形圧で125×250×75mmの直方体に成形し、これを2℃/hrでの昇温速度で1000℃に焼成して炭素材料を得た。

【0076】上記の試料から10×10×60mmの試料10枚を切り出した。これを実施例1と同様にして3点曲げ試験に供したところ、その平均曲げ強度は次の通りであった。

実施例 4      100MPa

【0077】又、上記の試料から5×30×1mmの試料を切り出し、これを陽極とし、Pt板を陰極、硫酸第2水銀を基準電極として、25℃の18M濃硫酸中で5mV/secの電位走査速度で電位走査して単掃引ボルタモグラムを求めた。その結果、電流密度が最大となり第1ステージの層間化合物生成に対応するピーク電位は1.4Vに観察され、電位走査を0~1.5Vの範囲で50回繰り返しても電極の破壊は見られなかった。

【0078】実施例 5

実施例4で得た炭素材から250×70×15mmの試料を切り出し、これを陽極として50Aスケールの電解槽にて陰極には鉄を用い、電解浴温度90℃、浴組成KF・2HFに厳密に保ちながら7A/dm<sup>2</sup>で定電流電解を行なった。その結果、この電極は3ヶ月以上割れることなく、またCF<sub>4</sub>含有量も常時10ppm以下に保たれた。

【0079】実施例 6

実施例4で得た炭素材から250×70×15mmの試料を切り出した。これらの試料の気孔率は7~8%で気孔の平均口径は1μm以下であった。これらの試料をそれぞれにつき以下の金属フッ化物系を用いて含浸処理を行なった: LiF、LiF+NaF(モル比1:1)、CsF+NaF(モル比1:1)、AlF<sub>3</sub>+NaF(モル比3:1)、MgF<sub>2</sub>、CaF<sub>2</sub>、NiF<sub>2</sub>+NaF(モル比2:1)。含浸処理は、金属フッ化物(又は混合物)をその溶融温度に加熱してから試料を溶融金属フッ化物

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(又は混合物)と加圧下で接触共存させ、気孔中に導入することにより行なった。

【0080】含浸処理の後には試料の気孔率はゼロとなり、細孔中に上記の金属フッ化物(又は混合物)が完全に含浸されている(充填率: 100%)ことが判明した。また曲げ強度も103MPaと、含浸による強度劣化が生じることなくむしろ曲げ強度が上昇した。

【0081】実施例 7

実施例6にて調製した金属フッ化物(又は混合物)含浸電極を陽極として50Aスケールの電解槽にて陰極には鉄を用い、電解浴温度90℃、浴組成KF・2HFに厳密に保ちながら電流密度7A/dm<sup>2</sup>で定電流電解を行なった。その結果、本電極は未含浸電極より0.5~1V浴電圧が低く、3ヶ月以上にわたって電解が安定的に継続した。また、生成フッ素中のCF<sub>4</sub>含有量も常時10ppm以下に保たれた。

【0082】

【発明の効果】上記の実施例からも明らかなように、曲げ強度が50MPa以上であって濃硫酸中での電位走査法により求めたボルタモグラムの第1ステージ層間化合物生成に対応する電流ピークの現われる電位が1.2V(硫酸第二水銀電極基準)以上であるとの2条件を満足する本発明の炭素電極は、電解中に破壊も崩壊も剥落も起こさず、そのため、長期間にわたって安定に電解操作することができるのみならず、所望の製品、例えばフッ素ガス中へのCF<sub>4</sub>の混入量も極めて低く、HF含有溶融塩電解用の電極として極めて有用なものである。

【図面の簡単な説明】

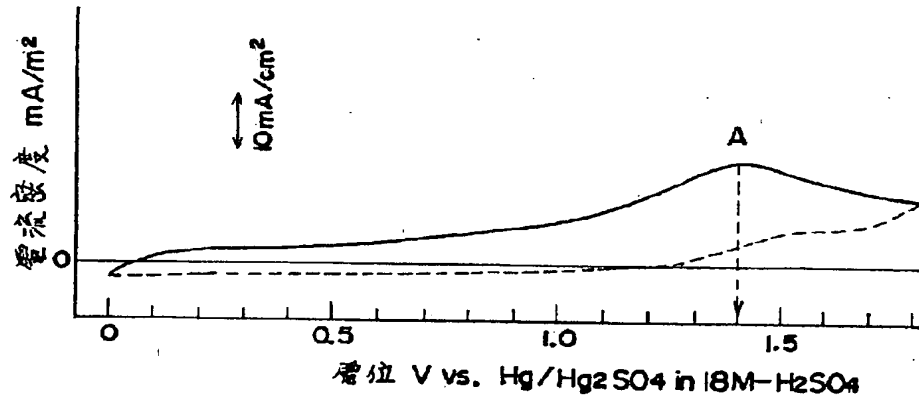
【図1】実施例1の本発明による炭素電極についての25℃濃硫酸中における電位走査速度5mV/secの電位走査により求めた単掃引ボルタモグラムを示した図である。

【図2】比較例1の炭素電極についての25℃濃硫酸中における電位走査速度5mV/secの電位走査により求めた単掃引ボルタモグラムを示した図である。

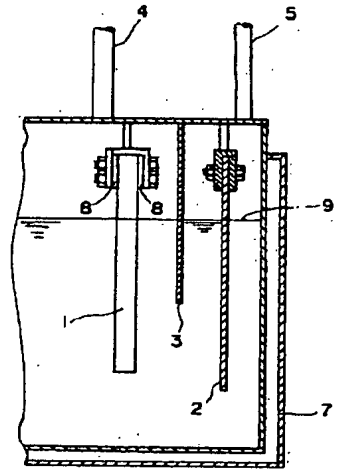
【図3】本発明の電解装置の一態様の内部を示す概略断面図である。

【図4】図3のIV-IV線に沿った概略断面図である。

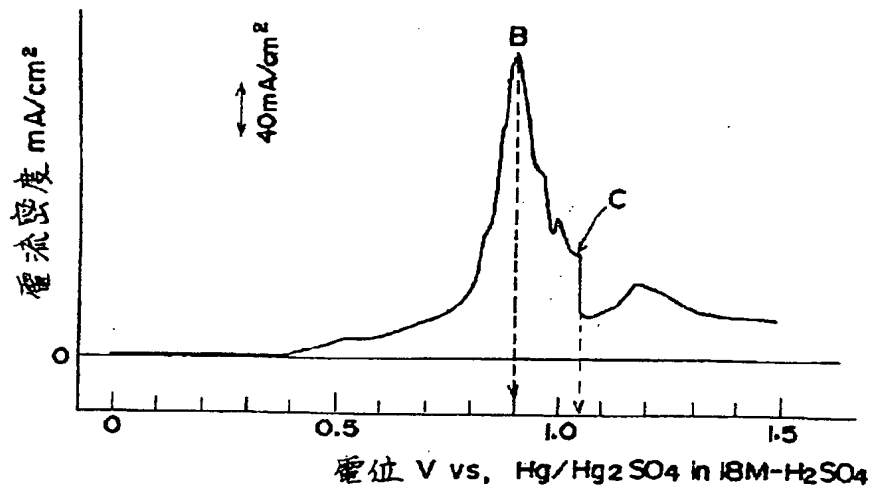
【図1】



【図4】



【図2】



【図3】

